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Numerical simulation reveals detailed kinetic effects in turbulent flames

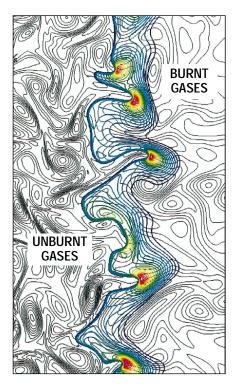
Tarek Echekki and Jacqueline Chen have been studying turbulent premixed methane-air flames modeled with reduced kinetics using the direct numerical simulation (DNS) approach. Since DNS provides spatially and temporally resolved combustion and turbulence information, Tarek and Jackie are using the DNS database to understand the fundamental interactions between turbulence and combustion. In addition, DNS provides the necessary statistics and closure information to validate and improve existing models of turbulent combustion.

Detailed chemistry mechanisms describing the combustion process of hydrocarbons typically include more than 100 reactions and 20 species. Until recently, DNS of turbulent combustion has been restricted to single-step Arrhenius kinetics with heat release and simplified transport models that reflect a single global Lewis number. Tarek and Jackie have developed a DNS tool that makes it feasible to incorporate reduced mechanisms for hydrocarbon combustion, thereby relating the flame structure to the underlying key elementary chemical kinetic steps. For methane-air flames, they use a four-step reduced mechanism that models the radical and fuel consumption and the oxidation of CO and H₂.

One objective of this research is to study the response of the turbulent flame to curvature and unsteady strain rate imposed by turbulence. Since flame curvature marks the gradients of scalars (species concentrations, temperature) within the flame, it is primarily coupled with the diffusion rates of mass and heat. Strain rate, which is a measure of flow gradients, affects the bulk gas transport in the flame. Better

knowledge of the sensitivity of species in the flame to curvature and strain rate in turbulent flames is needed to improve predictive models of turbulent combustion.

An example of the results obtained using DNS is seen from isocontours of the hydrogen atom (H) concentration overlaid on the vorticity field. Vorticity outlines the turbulent structures that distort the shape of the flame. In hydrocarbon flames, the H atom formed at an



Overlay of H atom concentration on vorticity magnitude isocontours. In the two-dimensional computation of a stoichiometric methane-air flame, the domain height is approximately 1 cm. The flame is propagating from right to left. Maximum values of the H concentration are indicated in red, minimum values in blue. The vorticity isocontours are in black.

intermediate stage in the reaction diffuses towards the fresh reactants and contributes to the breakup of the fuel in the thin fuel consumption layer. It is also a very light species that diffuses at a much faster rate than other reaction intermediates (differential diffusion). Differential diffusion for the H atom is amplified in the presence of flame curvature.

The image shows an increased concentration of H atom in flame elements that are convex towards the burnt gases. At these flame elements, differential diffusion coupled with flame curvature focuses the H atom towards the fresh gases and increases its concentration. The increase in H atom concentration results in an increase in the rate of fuel consumption and heat release.

Tarek and Jackie also investigated the response of another reaction intermediate, CO. The CO species' slower mass diffusion and oxidation rates increases its susceptibility to steady and unsteady strain rate effects, which is reflected in the modification of CO concentration profiles and in the reduction of heat release rates along strained flame elements. The different response observed in CO and H atom to flame curvature and unsteady strain rate illustrates the complex interaction of flame and turbulence in reacting mixtures.

Inge Gran (a visitor from the Norwegian Institute of Technology), Tarek, and Jackie have incorporated a detailed mechanism for the oxidation of methane into the DNS tool. This will enable them to study pollutant formation in hydrocarbon flames and the structure of various intermediate species that are assumed to be in steady state in the reduced mechanisms.

Unimolecular dissociation of formyl radical studied

The formal radical, HCO, plays an important role in determining the overall rate of hydrocarbon combustion. The fate of HCO is balanced between chain terminating reactions with other radicals (H, OH) and its unimolecular dissociation into H+CO, which is a primary source of H atoms and is therefore chain branching in character.

The dissociation of HCO is facile at flame temperatures because of the very weak C-H bond (~14 kcal/mol). Because of the slow rate of intramolecular vibrational energy redistribution and the low density of states above the dissociation threshold, the unimolecular decay of HCO does not adhere to commonly used statistical theories for unimolecular reactions. Indeed, the formyl radical provides a classic example of a sparse manifold of quasibound resonance states that exist above the dissociation threshold.

Recently, Joe Tobiason, Jim Dunlop, and Eric Rohlfing have measured the energies and widths of HCO resonances over a large range of energy and vibrational mode excitation. The team used a variety of laser-based spectroscopic techniques, including dispersed

fluorescence and stimulated emission pumping (SEP), detected either via fluorescence depletion (FD) or two-color resonant four-wave mixing (TC-RFWM) on the hydrocarbon flame band system of HCO.

Figure 1 displays examples of individual rotations lines observed in the SEP spectra of HCO resonances containing 6 to 12 quanta of C-O stretch excitation. The Lorentzian width of each line provides a direct measure of the dissociation rate from the resonance state. The pure C-O stretch resonances remain extremely narrow even at energies well above the dissociation limit; even with 12 quanta of C-O stretch the dissociation lifetime is 2.9 ps.

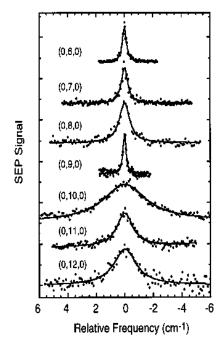
The HCO resonance widths (displayed in Fig. 2) are markedly mode specific. The narrowness of the pure C-O stretch resonances indicates the lack of coupling between the C-O stretch and the dissociation coordinate. Addition of bending excitation to the C-O stretch somewhat enhances the dissociation rate at high levels of excitation.

Clearly, the broadest resonances (and most rapid dissociation) are those in

which the C-H stretch motion is excited. The combination of bend plus C-H stretch is most effective at promoting dissocation, consistent with the nature of the minimum energy path for dissociation that involves motion along both the C-H and bending coordinates.

Joe, Jim, and Eric have compared their measured resonance energies and widths with a limited set of previous experimental measurements and with extensive calculations based on realistic potential energy surfaces (PES) derived from *ab initio* calculations. The resonance widths are particularly sensitive gauges of the unimolecular dissociation dynamics and provide stringent tests of theoretical potential surfaces.

The new experimental data on HCO has led to further refinements in a new theoretical PES for HCO, which is being developed in collaboration with Reinhard Schinke and co-workers at the Max-Planck-Institut für Strömungsforschung in Göttingen, Germany. The new PES provides significantly better resonance energies and widths, both for HCO and its isotopomer, DCO, than the previously accepted PES.



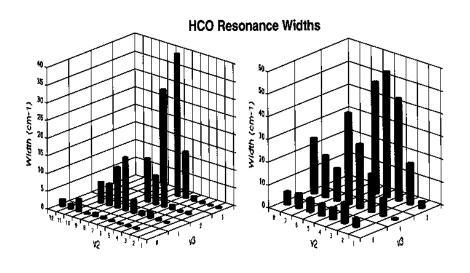


Figure 1. SEP spectra of a single rotational line for a series of HCO resonances with 6 to 12 quanta of C-O stretch. The (0,6,0), (0,7,0), and (0,8,0) spectra are TC-RFWM spectra; all others are FD-SEP spectra.

Figure 2. Observed resonance widths for HCO as a function of C-O stretch and bending quanta, v_2 and v_3 , respectively. Left: resonances with no C-H stretch excitation. Right: resonances with one quantum of C-H stretch.



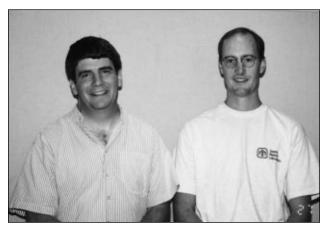
"Leading Women in Science" honor

Celeste M. Rohlfing was chosen by Sandia as one of 31 Department of Energy women from the National Laboratories profiled as Leading Women in Science at the United Nations Fourth World Conference on Women held in September in Beijing, China. Celeste specializes in combining chemical physics theory with high-performance computing to understand fundamental chemical reactions.



Keith Kaufman (left) visited the Burner Engineering Research Lab during testing on the International Flame Research Foundation's 300kW SCALING 400 burner. The test was used to gather a detailed data set from an industrial scale burner; the data will be used for model verification. Keith is shown with Phillipe Goix, Lloyd Claytor (EER), Pete Walsh (EER), and Neal Fornaciari (seated).

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Dirk Voelkel (right) from the Max-Planck Institut für Strömungsforschung in Göttingen, Germany, has just finished a one and a half-year visit with David Rakestraw. Dirk conducted laser diagnostic research in the Combustion Chemistry Department. His work focused on the development of spectroscopic techniques that utilize infrared laser radiation to measure transient chemical species in flames.



Aniefiok Akanatuk (left) from Babcock & Wilcox and Peter Bernath (center), professor at the University of Waterloo, are working with Larry Baxter on coal, biomass, and black liquor combustion and development of combustion diagnostics. Aniefiok is also pursuing a Ph.D. degree at Stanford University.



Steven Stolte (left) of the Free University of Amsterdam visited Dave Chandler to discuss their ongoing collaboration on combining molecular beam/hexapole state-selection techniques developed in Steven's laboratory with "ion imaging" techniques developed in Dave's. The combination of these techniques allows researchers to orient a molecule then photodissociate it, thereby learning more about the dynamics of the photochemical event.

Effect of fuel composition and excess air on toxic emissions studied

As part of a collaboration with the Petroleum Environmental Research Forum, Christopher Edwards and Philippe Goix have conducted experiments to assess the effect of fuel composition and excess air on air toxic emissions of small-scale industrial burners. This work is supported by the U.S. Department of Energy, Office of Industrial Technologies.

Among the amendments to the U.S. Clean Air Act made in 1990, a *Major Source* is defined as any site emitting 10 tons/year of any one species or 25 tons/year of all species combined. For example, a refinery of 250,000 barrel per day could become a *Major Source* if its effluents contain more than 100 ppb of benzene or toluene.

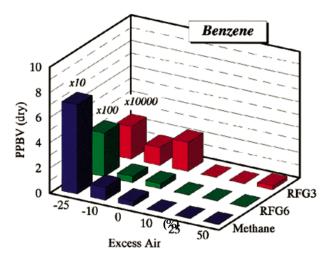
Chris and Philippe's experimental study established the furnace-out emis-

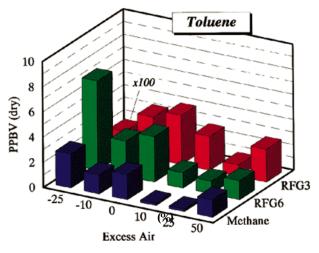
sions of air toxics compounds benzene, toluene, ethylbenzene, and the xylenes (BTEX) from a well-crafted, industrialstyle diffusion flame burner. Various excess air and fuel mixtures characteristic of the refinery fuel gas (RFG) used in refinery process heaters were studied. Methane was used both as a reference fuel and to represent the limit of hydrogen-free RFG. RFG6 and RFG3 are three-component blends of hydrogen, methane, and propane containing 1/6 and 1/3 hydrogen, respectively. Furnace-out emissions of the BTEX group were measured on-line using a gas chromatograph system with an iontrap mass spectrometer as a detector.

In order to achieve concentration measurements in the sub ppbv limit a preconcentrator using tenax as a sorbent was added to the system. The results show that benzene and toluene emission did not exceed 3 ppbv under the normal operating range of excess air (10–50%). Benzene and toluene increased by orders of magnitude at -25% excess air, with benzene emission being dominant by an order of magnitude.

At -25% excess air, all emissions increased dramatically when blended fuel RFG3 and RFG6 were used. This result is particularly important since *Major Source* emission levels are of order 100 ppbv for these species, and the *Residual Risk* level for benzene is estimated to be of order 10 ppbv.

The present measurements indicate that well-controlled, industrial-style diffusion flames of these RFG fuels do not produce BTEX emissions of concern with respect to the 1990 Amendments to the Clean Air Act.





Emission concentration measurements of benzene and toluene performed downstream in the combustion effluent for various excess air and RFG fuels. (For -25% excess air, multiply ppb by indicated factor.)



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